JET-COOLED CHLOROFLUOROBENZYL RADICALS: SPECTROSCOPY AND MECHANISM

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Whereas the benzyl radical, a prototypic aromatic free radical, has been the subject of numerous spectroscopic studies, halo-substituted benzyl radicals have received less attention, due to the difficulties associated with production of radicals from precursors. In particular, chloro-substituted benzyl radicals have been much less studied because of the weak visible emission intensity and weak C-Cl bond dissociation energy. The jet-cooled chlorofluorobenzyl radicals were generated in a technique of corona excited supersonic jet expansion using a pinhole-type glass nozzle for the vibronic assignments and measurements of electronic energies of the $D_1 \rightarrow D_0$ transition. The 2,4-,[a] 2,5-,[b] and 2,6-[c]chlorofluorobenzyl radicals were generated by corona discharge of corresponding precursors, chlorofluorotoluenes seeded in a large amount of helium carrier gas. The vibronic emission spectra were recorded with a long-path monochromator in the visible region. The emission spectra show the vibronic bands originating from two types of benzyl-type radicals, chlorofluorobenzyl and fluorobenzyl benzyl radicals, in which fluorobenzyl radicals were obtained by displacement of Cl by H produced by dissociation of methyl C-H bond. From the analysis of the spectra observed, we could determine the electronic energies in $D_1 \rightarrow D_0$ transition and vibrational mode frequencies at the D_0 state of chlorofluorobenzyl radicals, which show the origin band of the electronic transition to be shifted to red region, comparing with the parental benzyl radical. From the quantitative analysis of the red-shift, it has been found that the additivity rule can be applied to dihalo-substituted benzyl radicals. In this presentation, the dissociation process of precursors in corona discharge is discussed in terms of bond dissociation energy as well as the spectroscopic analysis of the radicals.

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